

Introduction: Major occurrences of hydrous alteration minerals on Mars have been found in Noachian impact craters formed in basaltic targets and detected using visible/near infrared (VNIR) spectroscopy. Until recently phyllosilicates were detected only in craters in the southern hemisphere [1,2]. However, it has been reported that at least nine craters in the northern plains apparently excavated thick layers of lava and sediment to expose phyllosilicates as well [3] and two Hesperian-aged impact craters, Toro [4] and Majuro [5], bear evidence of phyllosilicates in the southern highlands. Turner et al. 2015 [6] reported that hydrated minerals were identified in three Amazonian aged complex impact craters, located at 52.42°N, 39.86°E in the Ismenius Lacus quadrangle, at 8.93°N, 141.28°E in Elysium, and within Stokes crater. These discoveries indicate that Mars was globally altered by water throughout its past [7] but do not fully constrain formation conditions for phyllosilicate occurrences which have important implications for the evolution of the surface and biological potential of Mars.

Phyllosilicates associated with impact craters are believed to be present as a result of several processes which include impact excavation of older subsurface altered materials, impact-induced hydrothermal alteration in the central peak and rims of complex craters, and the formation of crater lake bed deposits (e.g. Gale crater) [8]. An example of impact-exhumed strata is proposed for phyllosilicate occurrences in the crater floor of McLaughlin, a 90 km diameter crater located at 21.9°N, 337.63°E and one of the deepest craters on Mars [9]. Turner et al. [6] argue for hydrothermal alteration in the central peaks of Amazonian complex craters as they contain alteration assemblages on their central uplifts that are not apparent in their ejecta. This same argument has been used to explain the presence of phyllosilicates that have been detected in central peaks of other impact craters [10] but with the caveat that a variety of syn-impact and post-impact degradation, hydrothermal alteration, and/or obscuration processes can occur [e.g., 11,12,13] making it difficult to decipher the dominance of processes manifest in various types of observations.

In terrestrial craters, a diverse suite of alteration minerals is observed as well [14]. In all settings where alteration products are associated with impact craters, the structural state of the components comprising the local terrain will influence the rate and extent of alteration through time because the rate of mineral dissolution is a function of the degree of crystallinity, surface area, and temperature.

Understanding the alteration assemblages produced by a range of conditions is vital for the interpretation of phyllosilicate spectral signatures which provide information about particle size and composition of geologic materials, to decipher the environment and evolution of early Mars, and espe-

cially for identifying habitable niches in which life could be initiated and sustained. The objective of this study is to conduct controlled Mars-like weathering experiments on experimentally shocked Mars analog material to produce a reference suite of samples for spectral analysis. These combined experiments will provide a means to identify martian alteration products and constrain alteration pathways. Naturally shocked materials from terrestrial impacts have inevitably already been altered and so are largely compromised for making similar comparisons; thus experimentation under controlled conditions is required.

Samples and Data Acquisition: The material chosen for the experiments is a well characterized natural sample of basaltic tephra (HWMK725) from Mauna Kea, Hawaii that was used in the laboratory-simulated acid-sulfate weathering experiments of [15]. Eight alteration experiments utilizing 100 mg aliquots of material (45-75 μm size fraction) and 20mL of fluid each (water/rock ratio = 200) were conducted to alter unshocked and shocked samples under neutral (de-ionized water) and acidic (0.1M H_2SO_4) fluids at 80°C and 160°C for 21 days. The samples were heated in general purpose Parr bombs with Teflon liners. The unaltered, altered, and altered shocked materials were then analysed at Johnson Space Center. VNIR reflectance spectra between 0.35 and 2.5 μm were acquired at ~25 °C with Analytical Spectral Devices (ASD) FieldSpec3 spectrometers configured with ASD Mug Lights in (humid) lab air. Spectralon (SRS-99-010; Labsphere, Inc.) was used as the reflectance standard. The spectra from the three detectors in the ASD instrument were spliced using software supplied with the instrument. A Scintag XDS 2000 X-ray diffractometer using Co-K α radiation operated at 45 kV and 40 mA current was used to characterize the mineralogy of randomized powder mounts over the range of 2 to 70° 2 θ .

Results: VNIR Spectra (Figure 1.) from samples (a), (b), and (c) have no detectable spectral features from OH and H_2O near 1.4 μm and (a) has no detectable vibration feature from H_2O at 1.9 μm . The samples altered in de-ionized water ((a) and (b)) have very low albedo compared to the acid altered samples (c) and (d). Increasing reflectivity for VNIR wavelengths greater than 0.75 μm in samples is due to increasing scattering with decreasing particle size in (c) and (d) resulting from shock comminution [16] and to an increase in a high albedo alteration product in (d) identified as alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) with XRD [16]. Sample (d) from the high temperature experiment (green trace) left an orange residue in the container after alteration consistent with the relatively sharp ferric absorption edge in the spectra extending from ~0.35 to 0.8 μm . Sample (d) (blue trace) has a feature near 0.44 μm that could be attributed to jarosite but jarosite was not identified in that sample by XRD, possibly

because it is present in an abundance below detection. EDS detected nano-phase iron-titanium-phosphorous blebs in the shocked and altered sample (d) (green trace) [16]. That phase was also not identified by XRD. Assignment of bands specific to overtone and combination tone vibrations is based on extensive literature on the subject [17] and references therein.

Conclusions: VNIR spectra are fairly featureless for samples altered under hydrolytic conditions versus those altered under sulfatic conditions. Sulfatic alteration is known to be more aggressive [18]. The samples altered at higher temperatures (160°C) are more highly altered than those altered at lower temperatures (80 °C) due to the increased rate of reaction expected at elevated temperature conditions. The shocked samples alter more readily than the unshocked samples likely due to structural deformation that increases reaction pathways and formation of amorphous material that is more easily attacked by fluids of any composition. Ehlmann et al., 2016 [19] report the first identification of alunite associated with impact deposits on Mars in Cross crater. Evidence for sulfatic alteration is present in many craters on Mars but the presence of alunite is evidence that the process is more extensive/complete. Results of these experiments show that alunite forms from acid sulfate alteration of shocked basalt at high temperature and high water/rock ratios and these conditions must have been present in Cross crater. It may be possible to discriminate between materials that exhibit alteration features expected from alteration of unshocked materials versus shocked materials and it has been observed that phyllosilicates associated with conical peaks and ejecta blankets on Mars are distinct from those on the surrounding plains. However, most of the Martian regolith has been impact gardened so VNIR spectral features identifying phyllosilicates from NASA's MRO-CRISM (Mars Reconnaissance Orbiter – Compact Reconnaissance Imaging Spectrometer for Mars) may reflect materials that have experienced accelerated alteration throughout their history as a result.

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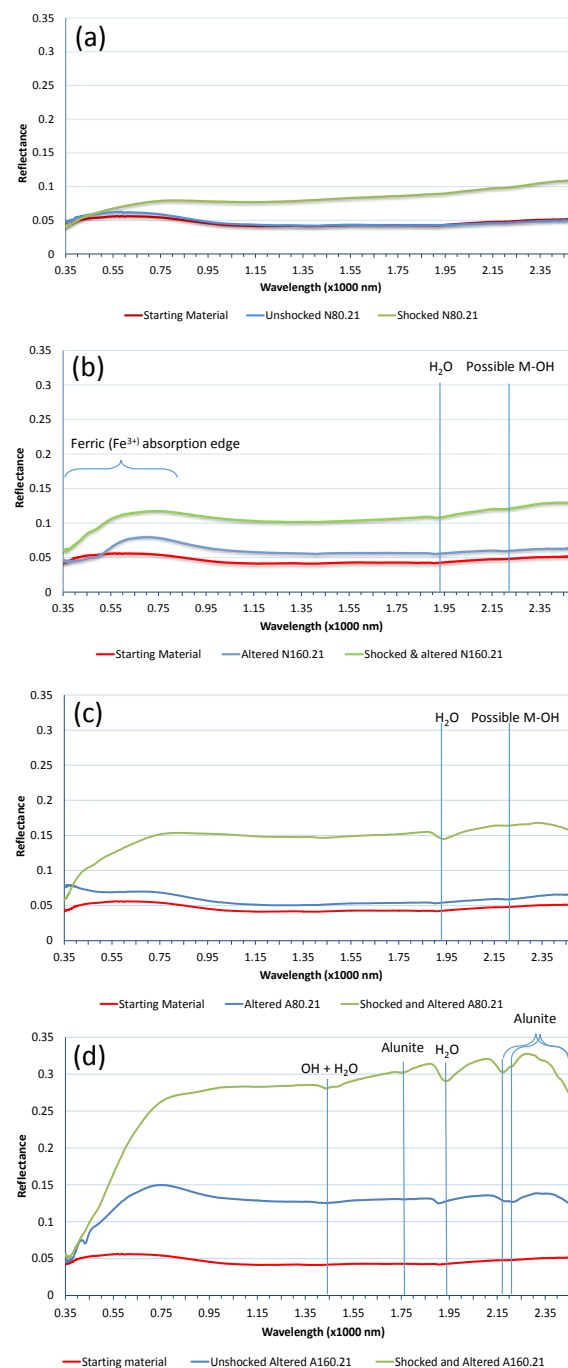


Figure 1. VNIR spectra of altered samples plotted with spectra of HWMK725 starting material for comparison. All alteration experiments were 21 days in duration. (a) Neutral fluid, T=80°C, (b) Neutral fluid, T=160°C, (c) Acid fluid, T=80°C, (d) Acid fluid, T=16°C. All charts are the same reflectance scale. Spectral feature locations are discussed in the text.